



## PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

The Patent Office  
Concept House  
Cardiff Road

Newport  
South Wales  
NP10 8QQ

PECOD 6 MAY 2003

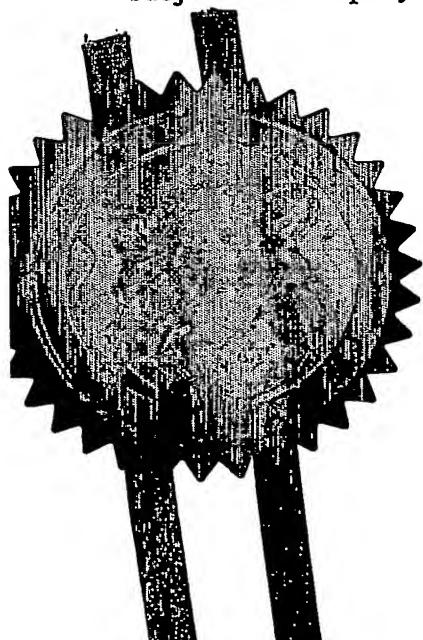
PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

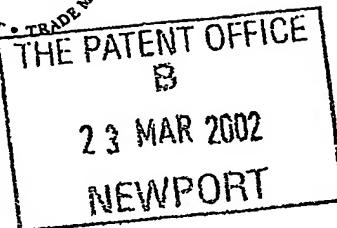


Signed

Dated

25 April 2003

BEST AVAILABLE COPY

25MAR02 E706076-5 D00355  
P01/7700 0.00-0206906.0**Request for grant of a patent**

*(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)*

The Patent Office

 Cardiff Road  
Newport  
South Wales  
NP10 8QQ

## 1. Your reference

W071366PGB

0206906.0

## 2. Patent application number

*(The Patent Office will fill in this part)*3. Full name, address and postcode of the or of each applicant *(underline all surnames)*
 The University of Birmingham  
Edgbaston  
Birmingham, B15 2TT  
England
Patents ADP number *(if you know it)*

798165002

If the applicant is a corporate body, give the country/state of its incorporation

England

## 4. Title of the invention

POWDER FORMATION METHOD AND APPARATUS

5. Name of your agent *(if you have one)*

Marks &amp; Clerk

"Address for service" in the United Kingdom to which all correspondence should be sent  
*(including the postcode)*

 Alpha Tower  
Suffolk Street Queensway  
Birmingham, B15 2TT  
England
Patents ADP number *(if you know it)*

18002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country

Priority application number  
*(if you know it)*Date of filing  
*(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
*(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

YES

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

*See note (d))*

**Patents Form 1/77**

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

- 
10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

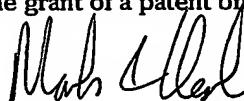
Request for substantive examination  
(*Patents Form 10/77*)

Any other documents  
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature



Date

22/3/02

12. Name and daytime telephone number of person to contact in the United Kingdom

David I WARD

0121 643 5881

**Warning**

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

**Notes**

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

## POWDER FORMATION METHOD AND APPARATUS

The present invention relates to a method and apparatus for the production of submicron powders.

There is an increasing demand for fine powders with particle size below 1  $\mu\text{m}$  for a range of applications including catalysis, low temperature sintering, solid rocket fuel, cold-gas spray coating and powder injection moulding, metallic paint and conducting paste. A powder with a particle size below 1  $\mu\text{m}$  has extremely high reactivity and can be accelerated to the same velocity as that of a transporting gas medium. These unique properties allow such powders to enhance (i) the rate of heat-release during burning for solid rocket fuel, (ii) spray coating at low temperature, and (iii) sintering kinetics at lower temperatures for the densification of powder materials.

Conventional industrial production of metal powders by such processes as reduction, decomposition and gas/water atomisation produces a wide size distribution from 2-500  $\mu\text{m}$  and a range of particle morphology from spherical to irregular. The weight fraction of particles with size below 2  $\mu\text{m}$  is usually below 5%. These conventional industrial processes therefore have a very low yield for fine powder particles and therefore are not economically viable for the large scale production of fine powder particles.

Alternative methods (e.g. inert gas condensation (IGC), chemical vapour condensation (CVC), mechanochemical processing, plasma atomisation and sonochemical synthesis) have been developed and have demonstrated successfully the production of nanosized metal powders. The IGC method involves evaporation of the material into its vapour state inside a vacuum chamber using either resistive heating, electron beam heating or a sputtering system. Above the evaporation

source is a cold finger, and a region of supersaturated metal vapour between the cold finger and the evaporation source, which nucleates small 'liquid-like' particles. The gas convection between the hot evaporation source and the cold finger transports the 'liquid-like' particles away from the evaporation source region. These particles then solidify onto the cold finger as ultrafine solid particles. Another variant of the IGC method involves the use of chemical vapour such as CVC rather than the physical vapour. All IGC-based methods require expensive vacuum systems or a chemical reaction chamber. Furthermore, such methods are currently limited to small batch production.

A non-vacuum based method (plasma atomisation) involves the melting and evaporation of a thin wire of material by a plasma torch. The vapour is then condensed by the inert gas around the plasma. Although the production yield of this method is high, the capital cost of the plasma torch and the necessary ancillary cooling systems can be very expensive. Furthermore, this method also requires an expensive powder handling system to protect the fine powder particles from exposure to air.

A mechanochemical processing method involves a reaction between an oxide powder and a reducing additive induced by high-energy ball milling. The method leads to the formation of by-products, which need to be removed by a subsequent purification process. Consequently, the mechanochemical processing method is expensive and gives a low yield of submicron sized powder.

The sonochemical synthesis of nanosized powder is based on the use of the acoustic cavitation phenomenon to decompose volatile solvent precursors to ultrafine solid powder particles. The sonochemical synthesis method is less widely applicable due to the need for volatile solvent precursors. In addition, several purification stages are required to extract the ultrafine powder particles.

It is an object of the present invention to provide an improved process for the production of submicron particle powders which obviate or mitigate one or more of the aforementioned disadvantages.

According to the present invention, there is provided a process for the production of submicron particles comprising the steps of :-

- (i) placing first and second electrodes in a volume of coolant, the electrodes being mutually spaced,
- (ii) passing an electrical current across the electrodes whereby to generate an electrical arc therebetween,
- (iii) maintaining a stable arc by controlling the relative spacing between the two electrodes to melt and separate material from at least one of the electrodes such that droplets of said material are formed, and
- (iv) quenching said droplets to form said submicron particles of the material in the coolant.

The current applied in step (ii) may be alternating or direct.

In a preferred embodiment, the electrodes are initially in contact when the electrical current is passed through them, the arc of step (ii) being created by moving them apart.

Suitable electrode materials (and hence the particles formed) include metals (eg. iron, tungsten, aluminium, titanium, magnesium and nickel), metal alloys (eg. low carbon steel, cast iron, TiAl, Ti-6Al-4V, stainless steel, tool steel, Fe-Ni-Co-Cr-Mo, Al-Cu-Fe-Mg-Si, Ni-Co-Cr-Fe-W, Cu-Ni, Cu-Sn, Mg-Al-Mn-Si and Co-Cr-Ni-Fe-Mo-W), graphite and other compounds, eg. carbides (such as SiC, WC), nitrides (such as  $\text{Si}_3\text{N}_4$ ), oxides (such as  $\text{PbTiO}_3$ ,  $\text{TiO}_2$  and  $\text{SnO}_2$ ) and metal hydrides (such as  $\text{MgH}_2$ ).

The coolant is preferably maintained at a temperature of less than 200 K, and more preferably less than 100 K. Most preferably, the coolant is liquid nitrogen (77 K).

The coolant may be inert (as in the case of liquid nitrogen). However a quantity of reactant may be mixed with an essentially inert coolant such that the material melted in step (iii) reacts with the reactant prior to being quenched in step (iv).

Preferably step (iii) is achieved by moving, preferably continuously, one of the electrodes relative to the other as material is melted.

During step (iii), relative rotation may be induced between the electrodes (eg. by rotating one of the electrodes) whereby to promote separation of the material from the electrode.

Said process may be a batch process, the particles being recovered after removal of the coolant (evaporation in the case of liquid nitrogen). It will be understood that the particles are protected from contact by air whilst contained within the coolant.

Alternatively, the process may be continuous, the method including a step of continuously passing coolant over the electrodes. In a particularly preferred embodiment, the particles are separated from the coolant after passing over the electrodes and the coolant is recycled back over the electrodes in a continuous circuit.

The present invention also resides in an apparatus for the production of submicron particles, said apparatus comprising:-

- (i) a sealable container for coolant,
- (ii) an anode and a cathode mounted within the container

- (iii) power supply means for passing a current between the anode and cathode, and
- (iv) adjustment means operably connected with at least one of the anode and cathode for controlling the spacing therebetween.

The anode and cathode may have the same or different chemical compositions.

Particularly preferred anode/cathode combinations are:-

graphite-graphite,

graphite-steel,

tungsten-steel, cast iron-cast iron,

aluminium-aluminium,

copper-copper,

titanium-titanium,

magnesium-magnesium and

stainless steel-stainless steel.

It will be understood that where the anode and cathode have different compositions, the submicron particle powder formed will have the composition of the anode, the cathode, a mixed composition or will be the product of the reaction between the two electrode materials. The exact composition of the powder depends, inter alia, on the current density (and hence temperature) of the arc and the melting points of the electrodes.

In addition, the anode or cathode may each comprise more than one material, such that, in use, generation of heat by the arc discharge causes the materials to react (solid or molten phase) before solidification.

Preferably, a supporting frame is provided for the anode, cathode and adjustment means, which components together with the supporting frame constitute an assembly which is removable from the container.

Preferably, said adjustment means comprises a rod connected to one of the anode and cathode (preferably anode), the rod extending to the anode or cathode through a wall of the container. The rod may be slideably mounted in the wall of the container, but is preferably screw-threadingly engaged therewith.

In one embodiment, sensing means is provided, the adjustment means and sensing means being operably connected such that in use, the adjustment means is automatically adjusted according to the output of the sensing means.

The sensing means may comprise a voltmeter for monitoring the voltage across the anode and cathode. Alternatively, the sensing means may comprise temperature sensing means to monitor the temperature of the arc. Indirect temperature sensing may be achieved using a spectrometer to monitor the intensity or wavelength of light produced by the arc.

The container may be provided with an inlet and an outlet for coolant. In a preferred arrangement, a coolant return circuit is provided between the outlet and the inlet, in which case the apparatus preferably also comprises a powder recovery region downstream of the container.

It will be understood that the invention also resides in a submicron powder produced according to the method or using the apparatus of the present invention.

An embodiment of the invention will now be described by way of example only with reference to the accompanying drawing which shows an apparatus in accordance with the invention.

Referring to Figure 1, a submicron powder producing apparatus comprises a sealable container 2 having a thermally insulated wall 4. A first electrode (cathode) 6 in the form of a rod is mounted on a copper block 8 at the base of the container 2 and extends upwardly towards a similarly shaped second electrode (anode) 10. The anode 10 extends downwardly towards the cathode 6 and is also mounted on a copper block 12 which in turn is suspended on a PTFE rod 14 which passes through the top wall of the container 2 and ends in a manually adjustable knob 16. The rod 14 and top wall are provided with cooperating screw threads such that the anode 10 can be raised or lowered by turning the knob 16. The relative positioning of the anode 10 and cathode 6 is stabilised by the provision of a PTFE support frame 20. The anode, 10 the cathode 6, the supporting blocks 8 and 12, the rod 14 and the frame 20 form a sub-assembly which can be raised or lowered out of or into the container as a unit. A dc power supply 22 capable of supplying up to 90A is provided externally of the container 2, and electrical connections are provided to the anode 10 and cathode 6 via the copper blocks 12, 8 to which they are mounted.

In use, the rod 14 is adjusted so that the anode 10 and the cathode 6 are in contact and the electrode sub-assembly is lowered into the container. The container 2 is then filled with liquid nitrogen and sealed. After thermal equilibration a dc current is applied to the electrodes 6,10 and the knob 16 is turned so as to introduce a gap between the electrodes 6,10 until an electrical discharge arc 24 is induced therebetween. Once the arc 24 is formed, the surface of the anode 10 and/or cathode 6 begins to melt and fragment into droplets, which are then quenched into fine (submicron) solid powder particles 26 by the surrounding liquid nitrogen. As a result, the spacing between the anode 10 and the cathode 6 is increased due to

removal of material from the anode 10 and/or cathode 6, thereby destabilising the arc 24. In order to stabilise the arc 24 during the continuous production of powders, the anode 10 is lowered by means of the knob 16. This helps to maintain a constant spacing between the anode 10 and the cathode 6, so as to maintain a stable arc 24.

After the process has been completed, the worn electrodes 6,10 and PTFE frame 20 are removed from the container 2 leaving the powder-containing liquid nitrogen. This can be poured into a storage container for subsequent use (the powder thereby being protected from air) or the nitrogen can be evaporated to leave free powder.

#### **Example 1**

Anode: 3 mm diameter graphite rod

Cathode: 6 mm diameter graphite rod

Current: 60 A, applied for 40 seconds.

Processing was carried out using the apparatus and method described above to give 5 g of carbon powder. Analysis by scanning electron microscopy (SEM) indicated substantially all the particles had a size of less than 1  $\mu\text{m}$  which were present as agglomerates.

#### **Example 2**

Anode: 3mm diameter Fe-0.08%C (steel) rod

Cathode: 6 mm diameter graphite rod

Current: 60 A, applied for 40 seconds

Processing was carried out as for Example 1 to give 1 g of a mixture of carbon and steel powders. Analysis by scanning electron microscopy (SEM) indicated that about 75% of the particles had a size of less than 1  $\mu\text{m}$ .

**Example 3**

Anode: 3 mm diameter Fe-0.08%C (steel) rod

Cathode: 3 mm diameter tungsten rod

Current: 60 A, applied for 25 seconds

Processing was carried out as for Example 1 to give 1 g of steel powder. Analysis by scanning electron microscopy (SEM) indicated that about 60% of the particles had a size of less than 1  $\mu\text{m}$ . The particle morphology was a mixture of spherical, agglomerate and irregular.

**Example 4**

Anode: 3 mm diameter Fe-2.5%C (grey cast iron) rod

Cathode: 6 mm diameter Fe-2.5%C (grey cast iron) rod

Current: 60 A, applied for 1 second.

Processing was carried out as for Example 1 to give 1 g of cast iron powder.

Analysis by scanning electron microscopy (SEM) indicated that about 20% of the particles had a size of less than 1  $\mu\text{m}$ . Substantially all the particles were spherical.

It will be understood that the particle size, size distribution and morphology can be controlled by variation in the current density, the time interval for arc discharge, the geometry and relative positioning of the electrodes, relative motion of the electrodes, electrode materials, temperature and nature of the coolant. For example, only about 20% of the particles were smaller than 1  $\mu\text{m}$  in Example 4. This is due to the relatively low melting point of the cast iron, which results in a larger melt volume at the electrodes which can not be rapidly quenched by the liquid nitrogen. It is anticipated that lowering the current (and therefore temperature) of the arc will reduce the melt volume, increase the rate of quenching and therefore increase the proportion of particles below 1  $\mu\text{m}$  in diameter.

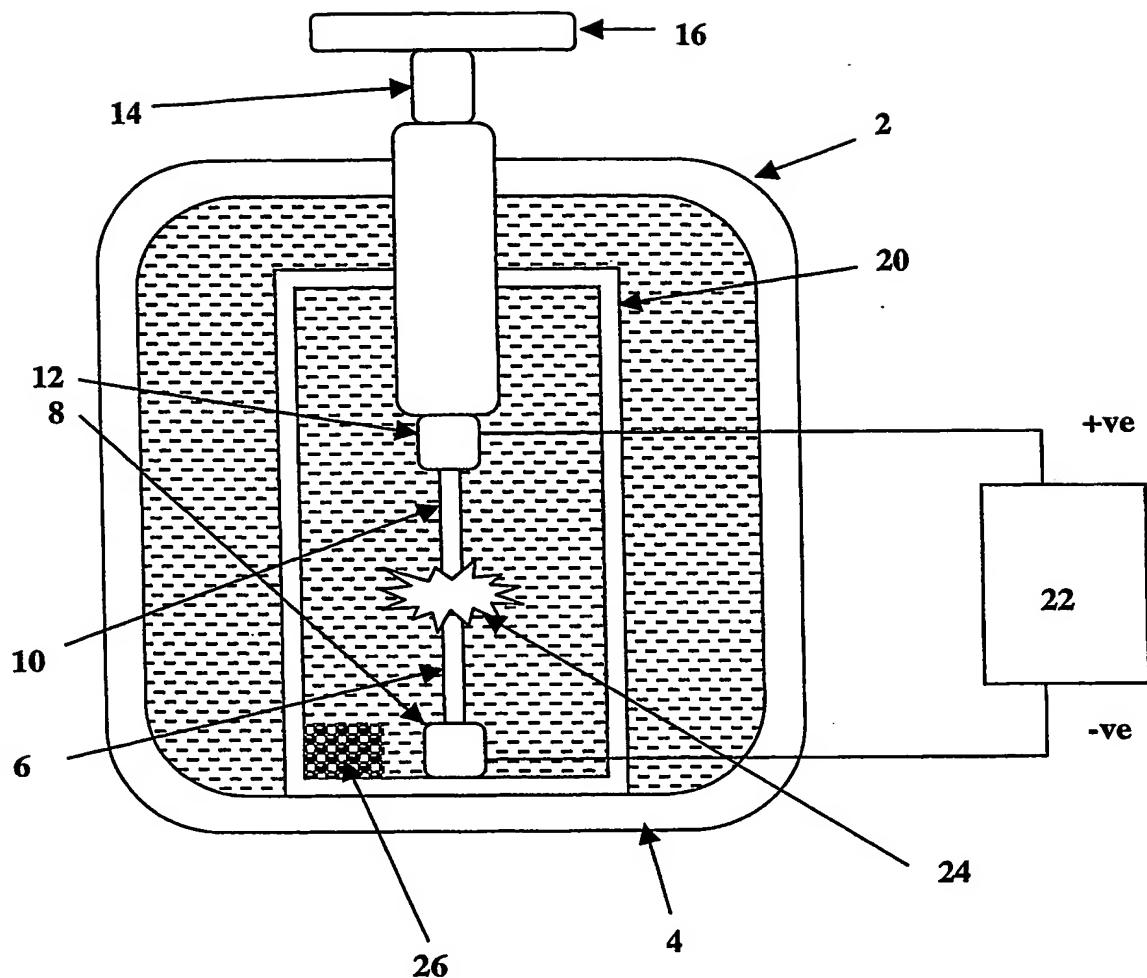
In a modification of the above apparatus (not shown), the anode is mounted on a spindle such that it can rotate about its longitudinal axis. This modification enhances the fragmentation of the melt by additional centrifugal force induced by the rotational motion.

In a further modification (not shown) the container is provided with an inlet and an outlet with additional pipe work connecting the two, thereby forming a continuous flow path through the container. A compressor and filtration unit is provided downstream of the outlet. In use, the liquid nitrogen evaporates on leaving the container through the outlet and carries with it the submicron powder. The powder is recovered in the filtration unit and the nitrogen returned to its liquid state by the compressor. This arrangement therefore allows continuous production of the powder until the anode requires replacement.

In yet a further modification, the dc power supply is replaced by an ac power supply. a.c. current causes the electrodes to undergo a cycle of melting and freezing which in turn limits the residence time interval of the melt. This in turn minimizes the volume of melt near the surface of the electrodes and allows the surrounding liquid nitrogen to quench the small volume of melt more effectively to produce a fine powder.

It will readily be appreciated that the arc discharge method of the present invention is not particularly limited to any particular technology and can be applied in a diverse range of applications where submicron powders are required. Such applications include solid rocket fuel (eg. Al-Al or Ti-Ti electrodes), catalysts (eg. Ni-Ni electrodes), conducting paste (eg. Cu-Cu electrodes), metallic paints (eg. Al-Al electrodes), hydrogen storage materials (eg. Mg-Mg electrodes), automotive powder metallurgy processed parts (eg. stainless steel-stainless steel electrodes), soft magnetic powder metallurgy processed parts (eg. Fe-Fe electrodes, thermite

welding (eg. Al-Al electrodes), cold-gas spray deposition (eg. tool steel-tool steel electrodes) and dyes.



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.